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Synthesis and Structure of a Hydrogenated Zinc Hemiporphyrazine†

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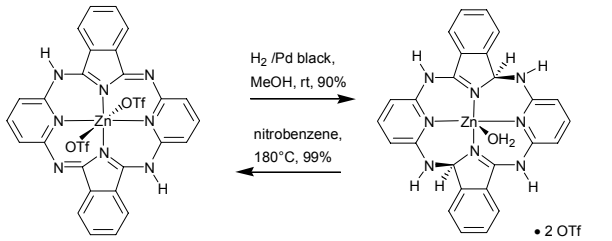
Palladium-catalyzed hydrogenation of an octahedral zinc trans-ditriflate hemiporphyrazine "$HpH_2Zn(OTf)_2$", furnishes a new macrocycle "$HpH_6Zn(OTf)_2$". This reaction is fully reversible upon heating in nitrobenzene, and the conversion is easily monitored by changes in color and fluorescence properties. The reversible cycling between these molecules may find future applications in hemiporphyrazine-based catalysts and/or hydrogen storage devices.

18 π electron phthalocyanines (Pcs) constitute some of the most important functional materials today. Initially used as dyestuffs, Pcs are also valuable components of catalysts, photovoltaics, data storage devices, photosensitizers, and chemical sensors.[1] The structurally related hemiporphyrazines (Hps), in contrast, have a non-aromatic 20 π electron skeleton with highly localized double bonds.[2] It is well known that hemiporphyrazines exhibit sensitivity to acid-mediated hydrolysis,[3] but little else is known about the fundamental chemical reactivity of the hemiporphyrazine macrocycle. While hemiporphyrazines can be elaborated by the introduction of substituents to the periphery during macrocycle formation,[4] direct modifications to the hemiporphyrazine macrocyclic "core" have not previously been reported. We hypothesized that, in contrast to Pcs, Hps should be reactive towards skeletal modifications due to their 20 electron π systems.

We recently reported the synthesis, structure, and photophysical properties of an octahedral zinc *trans*-ditriflate hemiporphyrazine complex "$HpH_2Zn(OTf)_2$" (Scheme 1, **1**).[5] In this complex, the charge of divalent zinc is balanced by axial triflate counterions, rendering the compound soluble in MeOH and other organic solvents.[5] In contrast to other metal-Hp complexes where the Hp serves as an anionic ligand,[6] $HpH_2Zn(OTf)_2$ contains a neutral Hp ligand with two protonated *meso*-nitrogen atoms. Bond length analyses of a high-resolution crystal structure indicated that these two positions possess delocalized enamine-like bonding (**N**···C···N) while the other bridging nitrogen atoms possess iminic (**N**=C) character.[5] This suggested that regioselective reactions could be achieved at the *meso* positions in a C_2-selective fashion. To test this concept, we evaluated the reactivity of **1** towards catalytic hydrogenation under a 1 atm H_2-atmosphere in the presence of palladium black. We speculated that the iminic *meso*-nitrogen sites would be highly reactive towards catalytic hydrogenation while the enamine-like *meso*-nitrogens would remain unmodified. Indeed, the reaction of **1** under an H_2-atmosphere in the presence of palladium black resulted in the addition of exactly two equivalents of H_2 to furnish the new crystalline material zinc tetrahydro-hemiporphyrazine "$HpH_6Zn(OTf)_2$" (**2**) (Scheme 1). Complex **2** is stable towards atmospheric oxidation in the solid state and can be handled in the presence of trace water without decomposition. Elemental analysis of **2** indicated that the product was obtained as a monohydrate.‡ ^{1}H-NMR spectra collected in d_6-DMSO indicate that $HpH_6Zn(OTf)_2$ (**2**) was generated as a single diastereomer having C_2 symmetry (Figure 1). ^{1}H-NMR analysis also indicates the presence of two distinct sets of *meso*-nitrogen hydrogens with enamine-like N-H resonances at 11.4 ppm, and amine-like resonances at 8.5 ppm (Figure 1). According to time-dependent NMR measurements, **2** in DMSO is stable at room temperature in the presence of atmospheric oxygen for days. However, in the presence of nitrobenzene at 180°C, **2** is oxidized to the parent compound **1** in quantitative yield.



zinc *trans*-ditriflate hemiporphyrazine "$HpH_2Zn(OTf)_2$" (**1**)

rac-(zinc tetrahydro-hemiporphyrazine ditriflate hydrate) "$HpH_6Zn(OTf)_2$" (**2**)

Scheme 1: Synthesis and oxidation of $HpH_6Zn(OTf)_2$ (**2**).

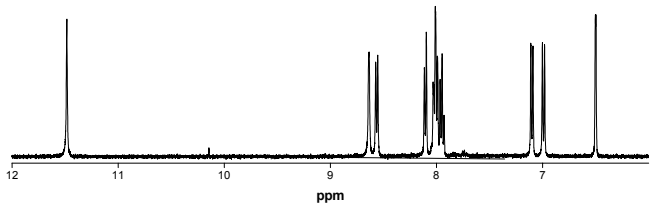


Fig. 1 ^{1}H-NMR spectrum of $HpH_6Zn(OTf)_2$ (**2**) in d_6-DMSO. See electronic supporting information for a full assignment of the spectrum.†

Crystals of **2** suitable for crystallographic characterization were grown from methanolic solutions by slow diffusion of diethylether/pentane (1:1). X-ray diffraction analysis of a single crystal revealed that two equivalents of H_2 had been added co-facially to give a saddle-shaped $HpH_6Zn(OH_2)•(OTf)_2$ macrocycle. The axial position of the 5-coordinate zinc ion is occupied by a water molecule that acts as O-H•••O hydrogen bond donor to the triflate counterions (omitted for clarity in Figure 2) (H•••O = 1.98(3) Å). Bond length analysis confirms reduction at the two iminic *meso*-nitrogen positions. The relatively short **N**=C bonds of 1.274 (2) Å present in the starting material (**1**),[5] have been replaced by N4-C1 bonds of 1.433(2) Å in **2**. In contrast, the N1-C4 and C4-N2 bonds of 1.308(2) Å and 1.338(2) Å in **2** are nearly identical in length to the enamine-like (**N**···C···N) bonds present in the starting material (**1**): 1.328(2) Å and 1.331(2) Å.[5]

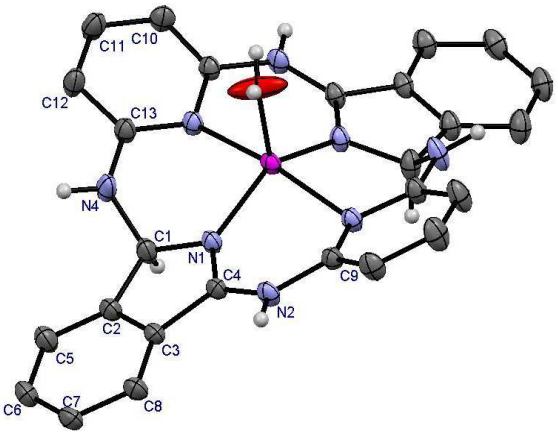


Fig. 2 Crystal structure of $HpH_6Zn(OH_2)•(OTf)_2$. The triflate counterions and selected hydrogen atoms have been omitted for clarity. 50% displacement ellipsoids are shown.

Hydrogenation of **1** reduces the extent of π-conjugation within the macrocyclic scaffold, resulting in a large color change. The hydrogenation reaction can therefore be monitored by simple visual inspection, as the red starting material (**1**) is converted to the yellow product (**2**). To further characterize these changes, the absorbance spectra of **1** and **2** were recorded in DMSO (Figure 3). DMSO was selected as the solvent because it is known to prevent aggregation of compound **1**.[5] Indeed, both **1** and **2** were found to obey Beer's law from 4 μM – 200 μM in DMSO. Similar to other reported hemiporphyrazines,[7] **1** exhibits a very broad, yet weak, absorption band centered at 530 nm. While the origin of this absorbance remains unknown,[7] it is either absent or greatly diminished and blue-shifted in **2**. This suggests that the transitions in this region involve the extended conjugation of the Hp macrocycle (**1**). Likewise, the $S_0 \rightarrow S_2$ transitions from 350 – 400 nm present in **1** are absent or greatly diminished and blue-shifted in **2** (Figure 3).

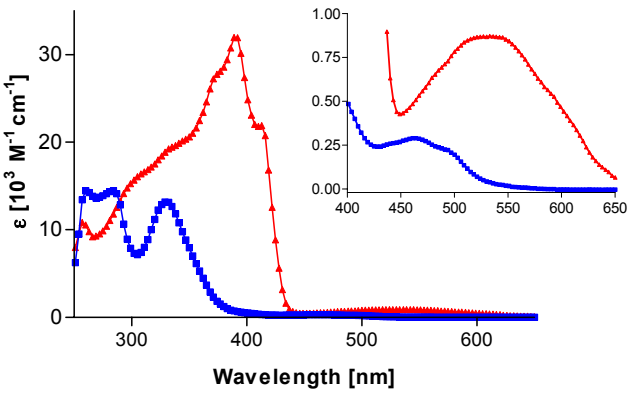


Fig. 3 Absorbance spectra of $HpH_2Zn(OTf)_2$ (red) and $HpH_6Zn(OTf)_2$ (blue) obtained in DMSO. These spectra obey Beer's law from 4 μM – 200 μM.

To our surprise, an apparent red-shift in luminescent emissions was observed following hydrogenation of **1**. Figure 4 shows the excitation and emission spectra of **1** and **2** collected in DMSO. Similar to the changes in absorbance (Figure 3), a blue-shift in the excitation spectrum of **2** was observed as compared to **1** (Figure 4). In contrast, the emission spectra exhibit the opposite trend, resulting in a large Stoke's shift for compound **2**. Upon excitation at 350 nm, the parent compound **1** gives emissions centered at 420 nm which are thought to result from emissive S_2 states (Figure 4).[5] Previous studies have suggested that aggregated hemiporphyrazines and aromatized analogs can exhibit emissions from S_1 states ranging from 550 – 700 nm.[5,8] Compound **2**, in contrast, exhibits a broad emission peak centred at 460 nm, probably from emissive S_1 states.

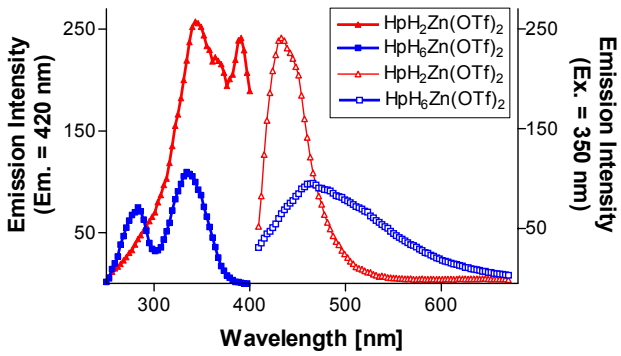


Fig. 4 Excitation (filled symbols) and emission spectra (empty symbols) of $HpH_2Zn(OTf)_2$ and $HpH_6Zn(OTf)_2$ prepared at 50 μM in DMSO. Emission spectra were collected using excitation at 350 nm and excitation spectra were collected by monitoring the emission at 420 nm.

In summary, we have reported the first synthesis and X-ray crystal structure of a core modified zinc tetrahydro-hemiporphyrazine ($HpH_6Zn(OTf)_2$). In the presence of H_2 and palladium black, $HpH_2Zn(OTf)_2$ consumes two equivalents of hydrogen in a C_2-selective fashion. Upon heating the product in the presence of nitrobenzene, $HpH_6Zn(OTf)_2$ is oxidized to the starting material in quantitative yield. The reversible addition and removal of hydrogen from $HpH_2Zn(OTf)_2$ is easily monitored by changes in its color and fluorescence properties. The reversible cycling between these molecules might find future applications in hemiporphyrazine-based reduction/oxidation catalysis and/or hydrogen storage devices.

Notes and references

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‡ Synthesis and characterization of **2**: **1** (300 mg, 0.37 mmol) and Pd black (3 mg, 0.03 mmol) were stirred in methanol (2 ml) under a 1 atm H_2-atmosphere at 25 °C for 2 h. Pd black was removed by filtration over celite and the methanol volume was reduced to 1 mL under reduced pressure. The remaining solution was layered with diethylether/pentane (1:1, 0.5 ml). The resulting yellow crystals were isolated by filtration and washed with diethylether and CH_2Cl_2 to afford **2** as yellow crystals (278 mg, 90%). ^{1}H-NMR (400 MHz, d_6-DMSO) 11.36 (s br, 2 H), 8.52 (d, J = 2.7, 2 H), 8.44 (d, J = 7.6, 2 H), 7.98 (d, J = 7.3, 2 H), 7.91 – 7.81 (m, 6 H), 6.98 (d, J = 7.9, 2 H), 6.87 (d, J = 8.3, 2 H), 6.34 (d, J = 2.5, 2 H); ^{13}C-NMR (100 MHz, d6-DMSO) 160.84, 158.58, 150.86, 144.79, 141.77, 132.43, 131.63, 130.07, 124.79, 123.07, 108.03, 105.14, 75.93; Elem. Anal. for $C_{28}H_{22}F_6N_8O_7S_2Zn$: C 40.71, H 2.68, N 13.57; found C 40.56, H 2.75, N 13.44. Crystal data for **2**: M = 826.02, monoclinic, space group *C*2/*c*, *a* = 20.9506(3), *b* = 10.1673(1), *c* = 16.0497(2) Å, β = 107.343(1)°, V = 3263.34(8) Å^3, *T* = 160 (1) K, *Z* = 4, D_c = 1.681 g cm^{-3}, μ = 0.975 mm^{-1}, 21655 collected reflections, 4547 independent reflections ($R_{(int)}$ = 0.021), $R(F)$ = 0.0351 for $I > 2\sigma(I)$ reflections, wR = 0.1009 for all data, S = 1.060, $\Delta\rho_{max}$ = 0.80 e Å^{-3}, Oxford Diffraction SuperNova diffractometer with Mo $K\alpha$ radiation, λ = 0.71073 Å.

‡ Synthesis and characterization of **1**: **2** (10.0 mg, 0.012 mmol) in nitrobenzene (5 ml) was stirred under N_2 at 180 °C for 3 h. The solution was cooled to room temperature and the resulting red solid $HpH_2Zn(OTf)_2$, **1** (9.8 mg , 0.012 mmol, 99%) was isolated by vacuum filtration and dried in vacuo. The analytical data matched those previously published.[5]

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